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Chemistry of 1-Carbena-5-hexyne and Related Intermediates

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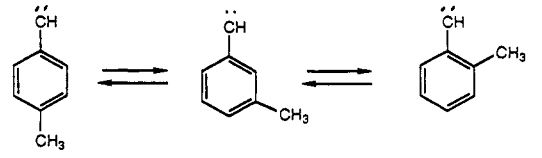
Pyrolysis of the lithium salt of the tosylhydrazone of 4,4-dimethyl-6-heptyn-2-one (**6b**) as the dry salt over a temperature range of 150 to 200 °C formed 4,4-dimethyl-1-hepten-6-yne (**8**), *cis*-4,4-dimethyl-5-hepten-1-yne (**9**), and *trans*-4,4-dimethyl-5-hepten-1-yne (**10**) with an average acyclic enyne composition of 11.1:4.9:84.0. The fourth product component, 1,5,5-trimethyl-1,3-cyclohexadiene (**11a**), was formed in 22–28% relative to the acyclic enyne fraction. In order to test for a carbene to carbene equilibration, the lithium and sodium salts of 3,5,5-trimethyl-2-cyclohexenone tosylhydrazone were pyrolyzed. The lithium (sodium) salt formed 95.2% (96.7%) **11** and 4.8% (3.3%) 5,5-dimethyl-1-methylene-2-cyclohexene (**19**). Pyrolysis of the sodium salt of 4,4-dimethyl-6-heptyn-2-one (**6c**) generated an increased amount of cyclic product exhibiting a product composition of 72.0% **11a**, 8.7% **8**, 2.3% **9**, and 17.0% **10**, whereas the pyrolysis of **6c** in the presence of 3.0 equiv of LiBr produced a product composition poorer in cyclic product (34.6% **11a**, 13.2% **8**, 5.2% **9**, and 47.2% **10**). Thermolysis of the lithium (sodium) salt of the tosylhydrazone of 2-heptanon-6-yne generates products with a reaction composition of 4.8% (47.8%) 1-methyl-1,3-cyclohexadiene (**11b**), 8.1% (5.9%) 1-hepten-6-yne (**21**), 29.9% (11.4%) *cis*-5-hepten-1-yne (**22**), and 57.3% (35.1%) *trans*-5-hepten-1-yne (**23**). In order to characterize the alkynylcarbenes formed in these decompositions, the related saturated systems were investigated by pyrolysis of the lithium and sodium salts of the tosylhydrazones of 2-heptanone and 4,4-dimethyl-2-heptanone. The mechanistic pathways for the decomposition of 2-diazo-4,4-dimethyl-1-heptyne are described in terms of (a) a pyrazole route and (b) a carbene to carbene rearrangement.

Carbene to carbene rearrangements are far less frequently encountered than analogous carbocation to carbocation or radical to radical rearrangements. In most instances, carbene to carbene rearrangements are more elaborate and may be illustrated by phenylcarbene to phenylcarbene (eq 1)[1] and ketocarbene to ketocarbene (eq 2) rearrangements,[2] as well as those we have proposed for potentially homoaromatic carbenes **1** and **3** (eq 3 and 4).[3,4]



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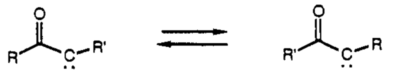

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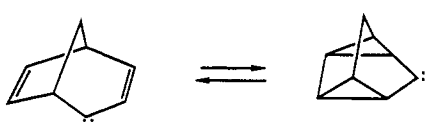

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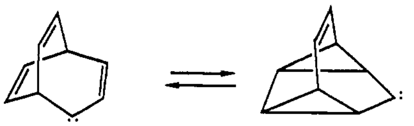

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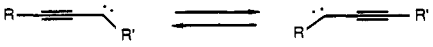
The chemistry of ethynylcarbene and closely related species[5] and the carbene degeneracy or carbene to carbene rearrangements (eq 5) which are conceivable for these intermediates provide a basis for an investigation into whether or not homologues might undergo a similar carbene to carbene rearrangement in a homoconjugate sense (eq 6). In this report we present results on species related to the hexynylidene intermediate (**5**).



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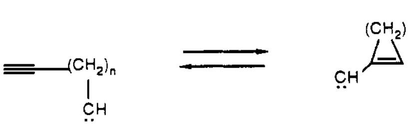

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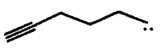

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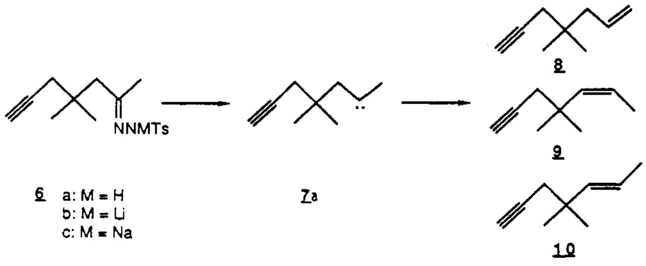
The hexynylidene system was initially represented by 2-carbena-4,4-dimethyl-6-heptyne (**7a**) and 2-carbena-6-heptyne (**7b**), since the tosylhydrazone precursors for these bivalent intermediates were easily prepared. In our initial experiments, 2-carbena-4,4-dimethyl-6-heptyne was generated by pyrolysis of the corresponding lithium salt (**6b**) (eq 7). It eventually became clear, however, that the ratios



(7)

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Table I. Regiochemistry of Hydride Migration in 2-Carbenaheptane and 4,4-Dimethyl-2-carbenaheptane

tosylhydrazone	method	yield, % 1-alkene	(*Z*)-2-alkene	(*E*)-2-alkene
	dry salt			
	Li, 150 °C	2.9 ± 1.2	34.6 ± 3.2	62.5 ± 2.3
	Li, 200 °C	3.5	26.6	69.9
	Na, 1.0 equiv, 150 °C	4.5 ± 2.2	18.9 ± 2.7	76.5 ± 2.6
	Na, 1.6 equiv, 150 °C	3.3	15.5	81.2
	solution			
	$NaOCH_3$, diglyme, heat	1.4	15.8	82.8
	photolysis			
	Li, THF	24.2	27.9	47.9
	dry salt			
	Li, 165 °C	7.0	11.8	81.2
	solution			
	$NaOCH_3$, diglyme, heat	1.6	trace	98.4
	photolysis			
	Li, THF	27.5	26.3	46.2

Table II. Pyrolytic Decompositions of the Lithium Salts of the Tosylhydrazone of 4,4-Dimethyl-6-heptyn-2-one

run	temp, °C	MeLi, equiv	**11a**	**8**	**9**	**10**
1	150	1.0	24.6 ± 5.6	9.4 ± 0.4 (12.5 ± 0.5[a])	4.3 ± 0.6 (5.7 ± 1.1)	61.7 ± 5.8 (81.9 ± 1.6)
2	166	1.0	21.7	6.7 (8.6)	2.7 (3.5)	68.8 (87.9)
3	200	1.0	23.2	8.5 (11.1)	3.2 (4.2)	65.1 (84.8)
4	200	1.0	28.1	8.8 (12.3)	4.3 (6.0)	58.8 (81.7)

[a] Values in parentheses are the acyclic alkene composition.

of alkenynes **8**, **9**, and **10** derived in these experiments would only reflect the carbene (or carbenoid) processes of interest, if great care were exercised in completely converting parent tosylhydrazone to lithium salt. In order to reach this conclusion and to understand the role that the alkynyl unit might play in reactions of carbene intermediates **7a** and **7b**, the chemistry of the related saturated species was evaluated.

Saturated Analogues: 2-Carbenaheptane and 2-Carbena-4,4-dimethylheptane

The tosylhydrazones of 2-heptanone and 4,4-dimethyl-2-heptanone were prepared from the readily available ketones and then decomposed thermally as the dry salt or in solution or photolytically in solution. The alkene distributions are summarized in Table I. In the case of the lithium salt of the tosylhydrazone of 2-heptanone, runs at 150 and 200 °C demonstrate that there is little temperature effect in the range 150–200 °C. The sodium salts were prepared by treating tosylhydrazone with sodium methoxide in methanol. Experiments with other tosylhydrazones seemed to indicate that a small excess of sodium methoxide increased the relative amount of the 1-alkene. The sodium salt was prepared with 1.0 and 1.6 equiv of base, and a consideration of the data for the pyrolysis of the dry sodium salt indicates that excess of base has little if any effect upon the alkene composition. Furthermore, the product composition obtained from pyrolysis of the dry sodium salt is very close to that obtained in solution. Thus, an interesting aspect of the chemistry of 2-carbenaheptane is that the product distribution found for the lithium salt is different from that obtained in runs with the sodium salt. It is known that lithium bromide will react with a diazoalkane to afford an organolithium intermediate which will react further.[6]

In the case of the sterically more encumbered intermediate, 2-carbena-4,4-dimethylheptane, the free carbene (generated only in solution) is more selective than the organolithium intermediate, while a comparison with free 2-carbenaheptane reveals that 2-carbena-4,4-dimethylheptane is clearly more selective, which is to be anticipated based on the greater interaction of *tert*-hexyl with methyl (versus butyl with methyl). The product composition for either of the photolytic cases illustrates that the product-determining intermediate is much less selective than in any of the thermal processes, and that in any case, photolytic or thermal, complexed or free, the product-determining intermediate forms alkenes in the anticipated ratio: *trans*-2- > *cis*-2- > 1-alkene.[7,8]

2-Carbena-6-heptyne and 2-Carbena-4,4-dimethyl-6-heptyne Systems

The lithium salt of the tosylhydrazone of 4,4-dimethyl-6-heptyn-2-one was prepared with special attention to achieving complete neutralization with methyllithium and the resulting salt pyrolyzed over the temperature range 150–200 °C (Table II). As runs 1–4 illustrate, the acyclic alkene composition is essentially constant over the temperature range and is in close correspondence with that for the saturated 2-carbena-4,4-dimethylheptane system (Table I).

The most important feature revealed in the lithium salt pyrolyses listed in Table II is the formation of cyclic product 1,5,5-trimethyl-1,3-cyclohexadiene (**11a**). Unfortunately, this does not prove that the cyclization occurs at the carbene stage. There are four possible stages in which cyclization may occur: (a) the tosylhydrazone stage, (b) the tosylhydrazone lithium salt stage, (c) the diazo compound stage, and (d) the carbene stage. Spectral analysis of the tosylhydrazones of 4,4-dimethyl-6-heptyn-

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(6) Goh, S. H.; Closs, L. E.; Closs, G. L. *J. Org. Chem.* **1969**, *34*, 25.

(7) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733.

(8) Yamamoto, Y.; Moritani, J. *Tetrahedron* **1970**, *26*, 1235.

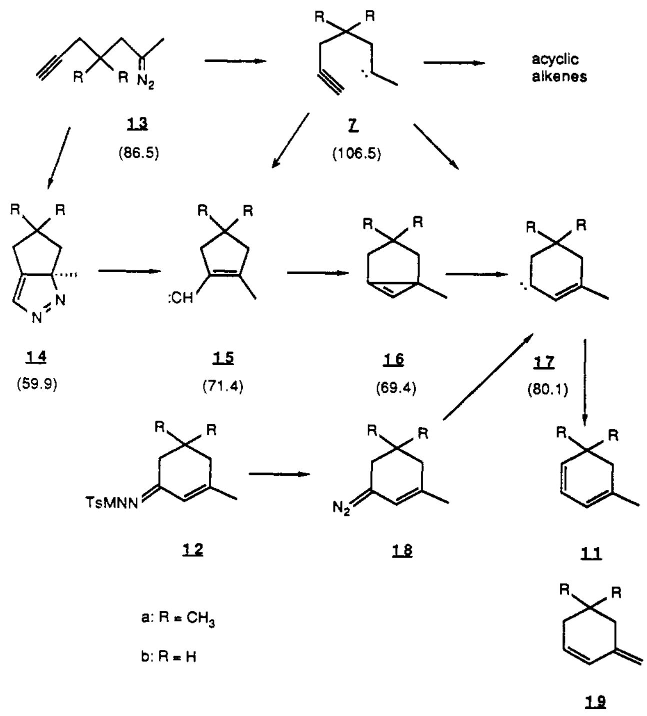
Table III. Pyrolysis of the Sodium Salts of 4,4-Dimethyl-6-heptyn-2-one in the Presence of Excess Sodium Methoxide or Lithium Bromide at 150 °C

	M	react condn	yield, %			
			11a	8	9	10
						
	Na	1.0 equiv of $NaOCH_3$	72.0	8.7 (31.1)[a]	2.3 (8.2)	17.0 (60.7)
	Na	1.2 equiv of $NaOCH_3$	74.6	8.2 (32.4)	1.6 (6.4)	15.5 (61.3)
	Na	1.0 equiv of $NaOCH_3$, 3.0 equiv of LiBr	34.6	13.2 (20.1)	5.2 (7.9)	47.2 (72.0)
	Li	1.0 equiv of LiBr	24.6 ± 5.6	9.4 ± 0.4 (12.5 ± 0.5)	4.3 ± 0.6 (5.7 ± 1.1)	61.7 ± 5.8 (81.9 ± 1.6)

[a] Percent acyclic alkene composition is presented in parentheses.

2-one (**6a**) and 3,5,5-trimethyl-2-cyclohexenone (**12a**, M = H) proved that cyclization did not occur in the preparation of the tosylhydrazone. Similarly, the lithium salts of these two tosylhydrazones (**6b** and **12a**, M = Li) were prepared, then dissolved in water; the parent tosylhydrazones were recovered by acidification (yields >90%). Spectral analyses of the recovered tosylhydrazones indicated that they were identical with starting materials. Extraction of the aqueous phase with pentane demonstrated that there were no additional products. It was assumed that cyclization takes place at either the diazo compound or the carbene stage. Diazo groups have been observed to add to an alkene unit in an intramolecular process,[9] and there is one instance of an intramolecular addition to a triple bond.[10] A reasonable mechanistic picture for reaction of the diazo compound **13a** is presented in Scheme I. The diazo compound might undergo intramolecular cycloaddition to form pyrazole **14a** which then could fragment to carbene **15a**, which could insert into the cyclopentene double bond to generated cyclopropene **16a**. Fission of the transannular bond in **16a** would lead to carbene **17a** and then by hydride migration to cyclohexadiene product **11a**. In competition with this process, carbene **7a** might be generated and undergo hydride migration to form acyclic alkenes. As an alternative to the pyrazole route to cyclic product **11a**, carbene **7a** could rearrange to bivalent **17a** directly or indirectly via **15a** (**7a** → **15a** → **16a** → **17a**) or via **16a** (**7a** → **16a**).

Scheme I



To test whether or not bivalent **17a** is in equilibrium with 2-carbena-4,4-dimethyl-6-heptyne (**7a**), **17a** was generated directly by pyrolysis of the lithium salt of 3,5,5-trimethyl-2-cyclohexenone tosylhydrazone (**12a**, M = Li). If carbenes **7a** and **17a** are in equilibrium, either directly or indirectly, then direct generation of carbene **17a** should produce the products arising from β-hydride migration. Pyrolysis of the lithium salt of 3,5,5-trimethyl-2-cyclohexenone tosylhydrazone (**12a**) produces a mixture of isomeric cyclic dienes: 95.2% 1,5,5-trimethyl-1,3-cyclohexadiene (**11a**) and 4.8% 5,5-dimethyl-1-methylene-2-cyclohexene (**19a**). Careful analysis by gas chromatography provided no evidence of the formation of acyclic alkenes 4,4-dimethyl-1-hepten-6-yne, and *cis*- and *trans*-4,4-dimethyl-5-hepten-1-yne (**8**, **9**, and **10**). Thus, carbene **17a** does not revert to bivalent **7a**, and if the rearrangement of **7a** to **17a** does occur, it is irreversible. In the pyrolysis of **12a** (M = Li), the minor product component (**19a**) was not formed by isomerization of the major component under the reaction conditions. Pyrolysis of sodium salt (**12a**, M = Na) provides a very similar outcome producing a mixture of **11a** and **19a** in a ratio of 96.7:3.3.

In the discussion above on the chemistry of the saturated carbene analogues, it was noted that lithium bromide has an effect on the product composition. In order to ascertain whether the presence of lithium bromide has an effect upon the product distribution in the pyrolysis of the salt of 4,4-dimethyl-6-heptyn-2-one tosylhydrazone, the sodium salt (**6c**) was prepared and pyrolyzed at 150 °C. The results are presented in Table III. There are two striking features: the increased amount of cyclization and the larger amounts of 1-alkene formed in the sodium salt pyrolyses. At first consideration, it seemed likely that the large amount of 1-alkene was due to excess sodium methoxide; however, a run carried out with a 20% excess of $NaOCH_3$ demonstrated that there was no effect upon the reaction composition. This is completely parallel to the observation listed in Table I, which demonstrates that a 60% excess has little or no effect on the alkene composition in the decomposition of the sodium salt of the tosylhydrazone of 2-heptanone. A consideration of the results of Table III suggests that reaction of intermediate

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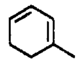
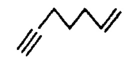
[9] Padwa, A.; Ku, H. *Tetrahedron Lett.* **1979**, 4425. Ojima, I.; Kondo, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1539. Kondo, K.; Ojima, I. *J. Chem. Soc., Chem. Commun.* **1972**, 63. Kirmse, W.; Grassmann, D. *Chem. Ber.* **1966**, *99*, 1746.

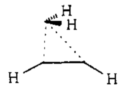
[10] Mykytka, J. P.; Jones, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 5933.

Table IV. Thermal and Photolytic Decompositions of Alkali Metal Salts of the Tosylhydrazone of 6-Heptyn-2-one

 NNMTs **24** →	 **19b**	 **25**	 **26**	 **27**
M = Li, 150 °C	4.8 ± 2.5	8.1 ± 0.3 (8.5 ± 0.5)[a]	29.9 ± 2.2 (31.4 ± 1.5)	57.3 ± 0.8 (60.2 ± 1.1)
M = Na, 150 °C	47.8 ± 2.2	5.9 ± 0.7 (10.9 ± 0.8)	11.4 ± 1.6 (21.8 ± 3.0)	35.1 ± 1.7 (67.2 ± 2.8)
M = Li, THF, hν	39.5	15.4 (25.4)	18.0 (29.8)	27.1 (44.8)

[a] Percent acyclic alkene composition is presented in parentheses.

diazo compound with lithium bromide produces a carbenoid which does not cyclize, the cyclic product arising by rearrangement of acyclic carbene **7a** to carbenacyclohexene **17a** and then by subsequent hydride migration to cyclohexadiene **11a**. The MNDO/(3 × 3) CI calculations of Jackson and O'Brien[11] on the related reaction of singlet methylene with acetylene reveal an "inward" transition state **20** and an "outward" second-order stationary point **21**. Owing to the intramolecular constraint in the presence case, an "outward" transition state (**22**) is required.



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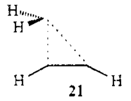

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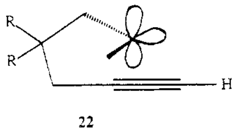

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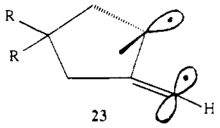

23

Jackson and O'Brien found that relaxation of **21** leads to a vinyl 1,3-diradical minimum with a perpendicular geometry analogous to **23**. A closed-shell calculation indicates that the vinyl 1,3-diradical can form cyclopropene with no energy barrier. In the present case, at the perpendicular 1,3-diradical point, one might expect ring strain to facilitate the formation of bivalent **15a** as the second intermediate in the sequence **7a**–**15a**–**16a**–**17a**, especially in view of the opportunity for relief of cis-1,3-diaxial methyl–methyl interaction.[12] Jackson and O'Brien view the pathway revealed from **21** to a perpendicular vinyl 1,3-diradical as unlikely because of the "crudeness of the MNDO approximation and the limited nature of the CI employed" and conclude, noting that Honjou et al.[13] found no evidence for a perpendicular vinyl 1,3-diradical minimum in their ab initio investigation of the singlet C_3H_4 energy surface, that there is no single-step pathway on the MNDO surface for conversion of singlet methylene plus acetylene to vinylcarbene (or the related perpendicular vinyl 1,3-diradical). It is important to note, however, in comparing the reaction of singlet methylene with acetylene to our system that in the 2-carbenaheptyne system the intramolecular nature of the process not only forces the reaction into the "outward" pathway, but eliminates the deep potential well for cyclopropene (41 kcal/mol relative to vinylcarbene in the singlet methylene + acetylene case). Alternatively the 2-diazoheptyne intermediate could cyclize to pyrazole **14a**, which upon loss of N_2 would form cyclopentenylcarbene **15a**, which might form bivalent **17a** via cyclopropene **16a**.

A consideration of the product array for the 2-carbena-6-heptyne intermediate (**7b**) provides a similar mechanistic picture. The results of the thermal and photochemical decompositions of alkali metal salts of the tosylhydrazones of 6-heptyn-2-one (**24**) are presented in Table IV. An acyclic fraction, consisting of 1-hepten-5-yne (**25**) and *cis*- (**26**) and *trans*-5-hepten-1-yne (**27**), and 1-methyl-1,3-cyclohexadiene (**19b**) are formed. As in the 4,4-dimethyl case, thermal decomposition of the sodium salt generates considerably more cyclic product.

The AM1 heats of formation[14] for the 4,4-dimethyl species are listed in Scheme I under the structural formulas (in kcal/mol) and are consistent with the pathways proposed. It should be noted that all pathways from acyclic carbene **7a** to products are exothermic, with the most economical pathway to cyclic product involving the direct rearrangement of **7a** to **17a**. If the pyrazole route is operative, the same product-determining intermediate, **17a**, seems to be the most reasonable possibility. An additional feature of importance in Table III is that, as the proportion of lithium salt is increased, the acyclic alkene composition changes with decreasing fractions of 1-alkene being produced, with the composition of acyclic alkenes for the pyrolysis approaching that observed with the lithium salt of 4,4-dimethyl-2-heptanone tosylhydrazone (Table I). The acyclic alkene distribution derived from the lithium salt pyrolysis of **24** is close to that observed for the saturated system (Table I); however, it is not clear that the acyclic alkene fraction formed by thermolysis of the sodium salt diverges to a greater extent from the saturated system (Table I). The acyclic alkene composition, then, for the free carbene derived from **13a** differs considerably from that which would have been anticipated judging by the alkene composition revealed for the pyrolysis of the sodium salt of 4,4-dimethyl-2-heptanone, while both **13a** and **13b** formed from the sodium salt generate sharply increased cyclic product relative to the corresponding lithium salt pyrolyses. Note that the alkene composition for the pyrolysis of the sodium salt of the 2-heptanone tosylhydrazone in solution is very close to that for the dry sodium salt pyrolysis. Perhaps the differences for the intermediates formed from the sodium and lithium salts are best explained by suggesting that, afterall, for the sodium salt pyrolyses, the carbena carbon of singlet carbene (**7a** or **7b**) is complexed in an intramolecular manner to the triple bond, which consequently alters the conformational picture and thus alters the product composition. The AM1 heats of formation suggest that, although the pyrazole may be an intermediate on the path to cyclic cyclohexadiene **11a** (**14a** → **15a** → **16a** → **17a** →

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[12] Elid, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley: New York, 1965; pp 50, 200.

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[14] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

11a), it is unlikely to contribute to the acyclic alkene fraction. In addition, we have a clear picture as to why carbenacyclohexene **17a** *generated from the corresponding* parent tosylhydrazone salt (lithium or sodium counterion) does not rearrange to acyclic alkynyl carbene **7a** to contribute to the acyclic alkene fraction.

Finally, it is of interest to note that the photolysis of the lithium salts of 2-heptanone, 4,4-dimethyl-2-heptanone, and 2-heptanon-6-yne tosylhydrazones generates an intermediate in each case which is much less selective than the corresponding intermediate formed in the pyrolyses of the lithium or sodium tosylhydrazone salt (Tables I and IV). In fact, the acyclic alkene ratios are strikingly similar and may be the consequence of the generation of a highly unselective excited-state singlet carbene or excited-state diazo compound as product-determining intermediate. We have proposed a similar explanation recently in our study of 4,4-diphenylcarbena-2-cyclohexene,[15] building on earlier studies of Chambers and Jones,[16a] Chang and Shechter,[16b] and Tomioka et al.[16c]

Experimental Section

General Methods. Melting points were determined using a Büchi melting point apparatus and are uncorrected. Boiling points are likewise uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B infrared spectrophotometer. Proton NMR spectra were recorded on Varian Associates EM-360 and FT-80A spectrometers; proton and carbon-13 spectra were run on a Varian FT-80A, a Bruker AC 300, or AM 400 spectrometer. High-resolution mass spectra were run on a CEC-2110B or a Kratos MS-50 TC mass spectrometer. Gas chromatography analyses were carried out on a Hewlett-Packard F&M 700 gas chromatograph equipped with a thermal conductivity detector. The following columns were utilized: (A) 14 ft × 0.25 in. aluminum containing 7% SE-30 on Chromosorb G AW 60/80 mesh; (B) 20 ft × 0.25 in. aluminum containing 20% tricresyl phosphate on Chromosorb P NAW 60/80 mesh; (C) 20 ft × 0.25 in. aluminum containing 5% Carbowax 20M on Chromosorb P NAW 60/80 mesh; (D) 10 ft × 0.25 in. aluminum containing 5% Carbowax 20M on Chromosorb P NAW 60/30 mesh; (E) 6 ft × 0.25 in. aluminum containing 8% SE-30 on Chromosorb W 60/80 mesh.

Product percentage yields calculated from GLC data are the average of at least three determinations and are uncorrected for differences in thermal conductivity among the different components in the mixture. Relative peak areas were measured with a Hewlett-Packard 3373B integrator except where noted. Products are listed in order of increasing retention times. Elemental analyses were performed by Chemalytics, Inc., 2230 South Industrial Park Dr., Tempe, AZ. Diethyl ether, diglyme, and tetrahydrofuran were used shortly after being distilled from sodium/benzophenone under nitrogen. All glassware described as dry was placed in an oven heated to 140 °C for at least 4 h, assembled while hot under a stream of nitrogen, and allowed to cool before use.

General Procedure for the Syntheses and Pyrolyses of the Tosylhydrazone Lithium Salts. In a dry, 100-mL, round-bottom flask equipped with a magnetic stirring bar, Claisen adapter, addition funnel, and condenser with gas inlet was dissolved a carefully weighed amount of the tosylhydrazone in 15 mL of dry tetrahydrofuran under nitrogen. The funnel was charged with a solution containing 1 equiv of methyllithium in diethyl ether using a dry syringe. The methyllithium was added dropwise to the well-stirred tosylhydrazone solution over a time period of 10–15 min and stirred for a further 15–30 min at room temperature. The stirring bar was retrieved; the solvent was removed using a rotatory evaporator and further dried by evacuating to 1–3 Torr (oil pump) and heating to 65 °C (oil bath) for 45–60 min. The flask was then connected to two (dry ice/isopropyl alcohol)-cooled traps connected in series, evacuated to 1–3 Torr, and heated (oil bath) to the desired temperature for 20–30 min. The volatile products were then collected from the traps and subjected to GLC analyses.

General Procedure for the Syntheses and Pyrolyses of the Tosylhydrazone Sodium Salts. In a dry, 100-mL, round-bottom flask equipped with a magnetic stirring bar, Claisen adapter, glass stopper, and gas inlet was placed 15 mL of absolute methanol under nitrogen. A carefully weighed amount of sodium metal was added. After all the metal had reacted, 5.0 mmol of tosylhydrazone was added in one portion and stirred at room temperature for 1 h. The stirring bar was removed and the solution was concentrated in the rotatory evaporator to about one-third to one-quarter of its original volume; then 10 mL of tetrahydrofuran was added and the solvent removed in the rotatory evaporator. The process was repeated with two more 10-mL portions of tetrahydrofuran. The dry sodium salt was dried further and pyrolyzed in the same manner as described for the dry lithium salt.

General Procedure for the Thermal Tosylhydrazone Decompositions with Sodium Methoxide in Diglyme. In a dry, 100-mL, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and gas inlet was dissolved 10.0 mmol of tosylhydrazone in 50 mL of dry diglyme under nitrogen. To the well-stirred solution was added 2.7 g (50.0 mmol, 5.0 equiv) of sodium methoxide in one portion. The solution was heated at 160 °C for 2 h, allowed to cool down to room temperature, poured into 300 mL of water, and extracted with 5 × 20 mL portions of pentane. The combined organic extracts were washed with 5 × 200 mL portions of water and dried over magnesium sulfate. The pentane solution was concentrated to about 3–5 mL by distillation through a 20-cm Vigreux column with a pot temperature of 50–55 °C. The concentrated solution was used for GLC analyses.

General Procedure for the Photolytic Decomposition of the Tosylhydrazone Lithium Salts. The lithium salt was prepared by allowing 2.50 mmol of tosylhydrazone dissolved in 50 mL of dry THF to react with a solution containing 2.50 mmol of methyllithium in diethyl ether under nitrogen in the same manner as described in the general procedure for pyrolyses of lithium tosylhydrazone salts. The solution was then transferred to a 2.0 × 25.0 cm quartz tube with a small magnetic stirrer and diluted with 25 mL of tetrahydrofuran to make a solution of 0.033 M in the salt. The tube was placed 2–4 cm from a Hanovia 450-W medium-pressure mercury lamp which was placed inside a quartz, water-cooled immersion well equipped with a Pyrex filter. The reaction tube was connected via a Drierite-filled trap to an inverted graduated cylinder filled with water to monitor nitrogen evolution. After the reaction was over, the solution was poured into 500 mL of water and extracted with 5 × 25 mL portions of pentane. The combined organic extracts were washed with 10 × 200 mL portions of water, dried over magnesium sulfate, and concentrated to 2–5 mL by distillation through a 20-cm Vigreux column with a pot temperature of 50–55 °C. The residue was analyzed by GLC.

Synthesis of 4,4-Dimethyl-2-heptanone. In a 500-mL pressure flask was dissolved 11.6 g (0.084 mmol) of 4,4-dimethyl-6-heptyn-2-one in 100 mL of methanol. To the solution was added 1.0 g of 10% palladium on charcoal. The reaction flask was attached to a Parr hydrogenation apparatus. The system was flushed three times with hydrogen. The reservoir was filled with 44.5 lb/in.^{2} pressure of hydrogen and the mixture was hydrogenated for 1.25 h (hydrogen uptake stopped after about 0.5 h of reaction) whereby the pressure had dropped to 32.0 lb/in.^{2} (hydrogen uptake was about 102% of calculated amount). The catalyst was removed by filtration and the solvent by distillation at atmospheric pressure. The residue was vacuum-distilled to yield 8.8 g (74%) of a clear liquid, bp 59–61 °C (12 Torr). The product had the following spectral characteristics: IR (neat) 1720 (carbonyl), 1395, 1385 (doublet) and 1160, 1150 cm^{-1} (*gem*-dimethyl); ^{1}H NMR (20% in $CDCl_3$) distorted triplet at δ 0.85 partially overlapped by a singlet at 0.90 (9 H, triplet is due to methyl protons of C-7 and singlet is due to *gem*-dimethyl protons), multiplet at 1.30 (4 H, methylene protons on C-5 and C-6), singlet at 2.15 (3 H, methyl protons of C-1), and a singlet at 2.35 (2 H, methylene protons of C-3).

Synthesis of 4,4-Dimethyl-2-heptanone Tosylhydrazone. In a 100-mL, round-bottom flask equipped with a magnetic stirring

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[15] Freeman, P. K.; Tafesh, A. M.; Clapp, G. E. *J. Org. Chem.* **1989**, *54*, 782.

[16] (a) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516. (b) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (c) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072.

bar and a reflux condenser was dissolved 5.6 g (0.030 mol) of tosylhydrazine in 30 mL of methanol by stirring the mixture in an oil bath heated to 56 °C. After the solid had dissolved, 4.3 g (0.030 mol) of 4,4-dimethyl-2-heptanone was added in one portion. The solution was stirred at 56 °C for 3 h and transferred to an Erlenmeyer flask; water was added until the mixture turned milky. After the solution had cooled down to room temperature, it was stored in the refrigerator overnight. The solid that had formed was collected by vacuum filtration and recrystallized from methanol to yield 6.8 g (72%) of white lumpy crystals, mp 78–80 °C. The product exhibited the following spectral characteristics: IR (solid film on sodium chloride plate) 3200 strong (amine proton), 1700 weak (imine), 1600 and 1500 (aromatic double bonds), 1395 and 1380 (*gem*-dimethyl), 1340 and 1170 (sulfonamide), 810 cm^{-1} (para-substituted benzene); ^{1}H NMR (20% $CDCl_3$ solution) singlet at δ 0.75 on top of a multiplet, 0.75–1.4 (13 H, the singlet corresponds to the *gem*-dimethyl protons and the multiplet to the protons on the propyl group C-5, C-6, and C-7), singlet at 1.8 (3 H, methyl protons on C-1), singlet at 2.15 (2 H, methylene protons at C-3), singlet at 2.45 (3 H, methyl protons on benzene), and a doublet of doublets at 7.3 and 7.8 (5 H, protons on benzene ring and proton on nitrogen buried underneath as evidenced by peak sharpening upon addition of D_2O). Anal. Calcd for $C_{16}H_{26}N_2O_2S$: C, 61.90; H, 8.44. Found: C, 61.94; H, 8.45.

Vacuum Pyrolysis of the Dry Lithium Salt of 4,4-Dimethyl-2-heptanone Tosylhydrazone. The title salt was prepared in the manner described in the general procedure by allowing 3.10 g (10.0 mmol) of tosylhydrazone suspended in 30 mL of dry ethyl ether to react with 6.0 mL of a 1.67 M methyllithium solution. The dry salt was pyrolyzed at 166 °C (0.10 Torr) to afford a red oil (turned clear overnight). The oil was analyzed by GLC on column A at 25 °C and a 60-mL/min flow rate and found to contain three products. By the use of heptane as an internal standard, the product composition was determined to be 4,4-dimethyl-1-heptene, 7.0%; *trans*-4,4-dimethyl-2-heptene, 81.2%; and *cis*-4,4-dimethyl-2-heptene, 11.8%. The yield of alkenes was 11.3% based on tosylhydrazone.

Thermal Decomposition of 4,4-Dimethyl-2-heptanone Tosylhydrazone with Sodium Methoxide in Diglyme. The tosylhydrazone (3.10 g, 10.0 mmol) was decomposed and worked up as described in the general procedure. The concentrate was analyzed by GLC on column A. By the use of heptane as an internal standard, the product was determined to contain 4,4-dimethyl-1-heptene, 1.6%; *trans*-4,4-dimethyl-2-heptene, 98.4%; and a trace of *cis*-4,4-dimethyl-2-heptene. The yield of alkenes was 51% based on tosylhydrazone.

Photolytic Decomposition of the Lithium Salt of 4,4-Dimethyl-2-heptanone Tosylhydrazone. The lithium salt was prepared as described in the general procedure by allowing 0.78 g (2.5 mmol) of tosylhydrazone to react with 1.5 mL (2.5 mmol) of methyllithium and photolyzing for 4.0 h. The solution was worked up and concentrated as described above. The residue was analyzed by GLC on column A. The product composition was determined to be 4,4-dimethyl-1-heptene, 27.5%; *trans*-4,4-dimethyl-2-heptene, 46.2%; and *cis*-4,4-dimethyl-2-heptene, 26.3%;, by using heptane as an internal standard. The yield of alkenes was 12% based on tosylhydrazone.

Stereochemical Integrity of the Alkene Products Derived from the Photochemical Decomposition of the Lithium Salt of 4,4-Dimethyl-2-heptanone Tosylhydrazone. The residue obtained from the decomposition of 4,4-dimethyl-2-heptanone tosylhydrazone with sodium methoxide in diglyme was shown by GLC to consist of 98.4% *trans*-4,4-dimethyl-2-heptene, 1.6% of 4,4-dimethyl-1-heptene, and a trace of *cis*-4,4-dimethyl-2-heptene. A 172.1-mg aliquot containing 63.4 mg of *trans*-4,4-dimethyl-2-heptene and 1.0 mg of 4,4-dimethyl-1-heptene was dissolved in 75 mL of dry tetrahydrofuran, photolyzed for 4.0 h, worked up, and concentrated in the same manner as described for the photolysis of the lithium salt of 4,4-dimethyl-2-heptanone tosylhydrazone. The reconcentrate was analyzed by GLC on column A. By using heptane as the internal standard, the residue was determined to consist of 0.9% 4,4-dimethyl-1-heptene and 99.1% *trans*-4,4-dimethyl-2-heptene. The recovery of alkenes was 33%.

Identification of Products from the Thermal Decomposition of 4,4-Dimethyl-2-heptanone Tosylhydrazone. The product from the thermal decomposition of the title compound showed three peaks upon GLC analysis on column B at 110 °C and a helium flow rate of 40 mL/min. Spectral data were obtained after isolating each product via preparative GLC. The first peak was identified as solvent (tetrahydrofuran) by comparison of retention times and proton NMR. The second peak was identified as a mixture of 4,4-dimethyl-1-heptene and *trans*-4,4-dimethyl-2-heptene from its spectral data: IR (neat) 3050 medium (vinyl hydrogen), 1650 weak (double bond), doublet at 1390 and 1370 medium (*gem*-dimethyl), 990 and 910 medium (1-alkene), and 970 cm^{-1} strong (trans alkene); ^{1}H NMR ($CDCl_3$, microcell) distorted triplet at δ 0.85 (methyl protons on C-7), singlet at 0.95 (*gem*-dimethyl), multiplet at 1.10–1.25 (methylene protons on C-5 and -6), doublet at 1.65 (methyl protons on C-1), and a multiplet at 5.25–5.35 (vinyl protons). That there is a small amount of another product (1-alkene) is indicated by the fact that some of the peaks are somewhat broadened. One can observe the following peaks: small doublet at δ 1.90 ($J \approx 8$ Hz, methylene protons next to double bond on C-3) and two multiplets at 4.9 and 5.0 and several small peaks between 5.20 and 5.60 (characteristic of a terminal alkene). The ^{13}C NMR spectra ($CDCl_3$, microcell) also indicates the presence of the above-mentioned compounds. The peaks assigned to 4,4-dimethyl-1-heptene are δ 17.5 (C-6), 27.1 (carbons of *gem*-dimethyls), 33.2 (C-4), 44.8 (C-5), 46.7 (C-3), 116.9 (C-1), and 136.0 (C-2). The following peaks were assigned to *trans*-4,4-dimethyl-2-heptene: δ 14.92 (C-7), 17.96 (C-1), 18.10 (C-6), 27.43 (carbons from the *gem*-dimethyls), 35.9 (C-4), 45.92 (C-5), 120.12 (C-2), and 141.59 (C-3). The peaks assigned to the 1-alkene were smaller than the ones from the trans isomer comparing similar carbon atoms. The peak assigned to C-7 of the 1-alkene was not observed. It could possibly be buried underneath the peak of C-7 of the trans alkene since these two carbons have the same calculated value for their chemical shift. When a mixture of the trans and 1-alkene was injected on column A, two peaks were obtained with the small peak being eluted first. Attempts to obtain pure samples of each isomer were unsuccessful owing to overlapping of the peaks in the course of preparative GLC. That the peak was indeed the 1-alkene and the large peak the trans alkene are confirmed by the following experiment. The overlapping peaks were collected in two ways. In the first one the whole peak was collected, an infrared spectra was recorded, and the ratio of the band at 970 cm^{-1} (trans alkene) to the band at 990 cm^{-1} was measured. In the second case, only about the latter 60% of the peak (i.e., the collected sample was enriched with the major component) was collected. After recording the infrared spectra, it was found that the ratio of the 970-cm^{-1} band to the 990-cm^{-1} band had increased considerably and thus proved that the major isomer was the trans alkene. The third peak was identified as *cis*-4,4-dimethyl-2-heptene: IR (neat) 3020 cm^{-1} strong (cis double bond); ^{1}H NMR ($CDCl_3$, microcell) distorted triplet at δ 0.90 (3 H, methyl protons on C-7), singlet at 1.10 (6 H, *gem*-dimethyl protons), multiplet at 1.25–1.45 (4 H, methylene protons on C-5 and -6), broad doublet at 1.70 (3 H, methyl protons, C-1), and multiplet at 5.20–5.35 (2 H, vinyl protons); ^{13}C NMR ($CDCl_3$, microcell) δ 14.23 (C-1), 14.99 (C-7), 18.14 (C-6), 28.98 (carbons of *gem*-dimethyl), 36.59 (C-4), 46.81 (C-5), 122.75 (C-2), and 139.96 (C-3). The products of the other reactions were identified by comparison of GLC retention times.

Synthesis of 4,4-Dimethyl-6-heptyn-2-one Tosylhydrazone. In a 200-mL, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was dissolved 12.7 g (0.0680 mol) of tosylhydrazine in 100 mL of methanol by stirring the mixture in an oil bath heated to 52 °C. After all the solid had dissolved, 9.4 g (0.0680 mol) of 4,4-dimethyl-6-heptyn-2-one[17] was added in one portion. The solution was stirred at 52 °C for 4.5 h, transferred to a 250-mL Erlenmeyer flask, and stored in the freezer overnight. The crystals that formed were collected by suction filtration to yield 14.2 g of small white crystals. A second crop of 2.8 g was obtained by dropwise addition of water to the mother liquor until it turned cloudy, storing the solution in the refrigerator, and collecting by suction filtration. A total of 17.0 g (82%), mp 105–6 °C, of crystalline material was obtained. The product exhibited the following spectral properties: IR (solid film on sodium chloride

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[17] Felix, D.; Schreiber, J.; Ohloff, G.; Eschenmoser, A. *Helv. Chim. Acta* 1971, *54*, 2896.

Table V

T, °C	A, %	B, %	C, %	D, %	yield, %
150	16.6	9.8	3.4	70.2	16
150	27.5	9.4	4.7	58.4	
150	29.4	8.8	4.2	57.5	
150	25.2	9.5	4.7	60.5	
166	21.7	6.7	2.7	68.8	22
200	23.2	8.5	3.2	65.1	16
200	28.1	8.8	4.3	58.8	12

Table VI

$NaOCH_3$, equiv	A, %	B, %	C, %	D, %	yield, %
1.2	75.9	7.1	1.1	15.9	27
1.2	73.3	9.4	2.2	15.1	15
1.0	69.1	10.5	3.4	17.1	30
1.0	74.9	6.9	1.2	17.0	28

plate) 3275 (ethynyl proton), 3200 (amine proton), 2110 (triple bond), 1640 (imine), 1600 (aromatic double bond), 1395 and 1380 (*gem*-dimethyl), 1340 and 1160 (sulfonamide), 820 cm^{-1} (para-substituted benzene); ^1H NMR (20% in $CDCl_3$) singlet at δ 0.9 (6 H, *gem*-dimethyl), singlet at 1.85 (3 H, methyl protons), singlet on top of multiplet at 1.95 (3 H, methylene protons of C-3 and ethynyl proton), singlet at 2.25 (2 H, methylene protons of C-5), singlet at 2.45 (3 H, methyl on benzene), and a doublet of doublets at 7.30 and 7.90 (5 H, aromatic protons and NH proton buried underneath as evidenced by peak sharpening upon addition of D_2O). Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.72; H, 7.24. Found: C, 62.58; H, 6.91.

Vacuum Pyrolyses of the Dry Lithium Salt of 4,4-Dimethyl-6-heptyn-2-one Tosylhydrazone. The title salt was prepared and dried as described in the general procedure by reaction of 1.53 g (5.0 mmol) with 3.6 mL (5.0 mmol) of 1.4 M methyllithium solution. The salt was then pyrolyzed at different temperatures and analyzed by GLC on column C at 65 °C and a 10-mL/min flow rate of helium employing benzene as an internal standard. The following products were obtained: 1,5,5-trimethyl-1,3-cyclohexadiene (A), 4,4-dimethyl-1-hepten-6-yne (B), *cis*-4,4-dimethyl-5-hepten-1-yne (C), and *trans*-4,4-dimethyl-5-hepten-1-yne (D). The relative amount of each product and the total yield of products based on tosylhydrazone are shown in Table V for the different reaction temperatures.

To test the stability of the products to the reaction conditions, a product fraction (27.5% **11a**, 9.4% **8**, 58.4% **10**, and 4.7% **9**) was added to the pot residue from the above reaction and the mixture heated at 150 °C for 2 min; the volatile fraction was then allowed to distill into a trap at 4 mm pressure. GLC analysis showed a composition of 24.4% **11a**, 10.0% **8**, 60.9% **10**, and 4.7% **9**. It should be noted that the observed reaction time in the original pyrolysis was less than 30 s.

Vacuum Pyrolyses of the Dry Sodium Salt of 4,4-Dimethyl-6-heptyn-2-one Tosylhydrazone. The salts were prepared and dried as described above using 1.53 g (5.0 mmol) of tosylhydrazone and pyrolyzed at 150 °C. GLC analyses give the results in Table VI.

Vacuum Pyrolyses of the Dry Sodium Salt of 4,4-Dimethyl-6-heptyn-2-one Tosylhydrazone in the Presence of Lithium Bromide. The salts were prepared and dried in the same manner using 5.0 mmol of tosylhydrazone and 5.0 mmol of sodium as in the preceding preparation with the exception that after adding the third portion of tetrahydrofuran, 1.3 g (15.0 mmol, 3.0 equiv) of lithium bromide was added; the drying procedure was continued without further change. The salts were pyrolyzed at 150 °C and analyzed by GLC. The results are given below.

A, %	B, %	C, %	D, %	yield, %
42.9	12.2	6.0	39.4	21
26.3	14.2	4.5	55.1	23

Chemical Confirmation of the Structure of the Lithium Salt of 4,4-Dimethyl-6-heptyn-2-one Tosylhydrazone. The salt was prepared in the same manner as previously described by reaction of 0.91 g (3.0 mmol) of tosylhydrazone with 1.7 mL of a 1.75 M solution of methyllithium (3.0 mmol) under nitrogen. The solution was stirred at room temperature overnight to allow most of the solvent to evaporate. The dryness of the salt was ensured by heating the flask at 52 °C (5 Torr) for 24 h. The dry salt was treated with 40 mL of water (all of the solid dissolved). The aqueous solution was acidified with 10 drops (acid to litmus paper) of 3 M sulfuric acid. The precipitate was collected by suction filtration to yield 0.80 g of a white, fluffy solid. An ^1H NMR of the product matched the one of the starting material, 4,4-dimethyl-6-heptyn-2-one tosylhydrazone. The percent recovery of the product was 89%.

Identification of Products from the Reactions of 4,4-Dimethyl-6-heptyn-2-one Tosylhydrazone. The reaction mixture of the decomposition of the title compound at 166 °C was resolved into three components on column D at 70 °C and a helium flow rate of 50 mL/min. The first peak was identified as 1,5,5-trimethyl-1,3-cyclohexadiene by comparison of its IR, ^1H, and ^{13}C NMR spectra with those of an independently synthesized sample. The second peak was identified as a mixture of 4,4-dimethyl-1-hepten-6-yne and *trans*-4,4-dimethyl-5-hepten-1-yne based on IR and NMR spectra: ^1H NMR ($CDCl_3$) δ 0.97 (s, 6 H *gem*-dimethyl of terminal alkene), 1.07 (s, 6 H, *gem*-dimethyl of trans alkene), 1.67 (d, 3 H, J = 5 Hz, terminal methyl of trans alkene), 1.98 (t, 1 H, J = 2 Hz; t, 1 H, J = 2 Hz; two triplets superimposed, isomeric alkyne hydrogens), 2.06 (m, 4 H, C-3, C-5 of terminal alkene), 2.13 (d, 2 H, J = 2 Hz, C-3 of trans alkene), 5.01–5.10 (2 vbs, 2 H, C-1, terminal alkene), 5.37–5.53 (m, 2 H, C-5, C-6, trans alkene), 5.79 (m, 1 H, C-2, terminal alkene). Decoupling resonance at δ 1.67 collapsed 5.37–5.53 to absorptions at δ 5.50 and 5.42 (dd, 1 H, 1 H, J = 15.6 Hz). HRMS, EI peak 1 for C_9H_{14} ($M^{\cdot+}$) calcd 122.1095, found 122.1096. Peak 2 was resolved into two peaks by capillary GC on a DB Wax column 2a (1-alkene) and 2b (trans 2-alkene); 2a, for C_8H_{11} ($M - 15^+$) calcd 107.0861, found 107.0858; 2b, C_8H_{11} ($M - 15^+$) calcd 107.0861, found 107.0880. The IR (neat) had the following bands: 3300 strong (ethynyl hydrogen), 3030 (vinyl hydrogen), 2125 medium (triple bond), 1650 weak (double bond), doublet at 1370 and 1390 (*gem*-dimethyl), 1000 and 920 medium (characteristic band of a terminal vinyl group), and 970 cm^{-1} strong (characteristic band for a trans alkene). A sample enriched in peak 2b was subjected to ^{13}C NMR ($CDCl_3$, microcell) showing the following peaks: δ 14.84 (C-7), 27.28 (*gem*-dimethyl carbons), 33.12 (C-3), 35.68 (C-4), 69.59 (C-1), 82.3 (C-2), 121.31 (C-6), and 139.98 (C-5) which corresponds to *trans*-4,4-dimethyl-5-hepten-1-yne.

The last peak from column D was identified as *cis*-4,4-dimethyl-5-hepten-1-yne from its spectral data: ^1H NMR ($CDCl_3$) δ 1.22 (s, 6 H, C-4, *gem*-dimethyl), 1.74 (d, 3 H, J = 6 Hz, C-7), 1.98 (t, 3 H, J = 2 Hz, C-1), 2.26 (d, 2 H, J = 2 Hz, C-3), 5.33–5.45 (m, 2 H, C-5, C-6); decoupling resonance at δ 1.74 yielded δ 5.41, 5.34 (dd, 1 H, 1 H, J = 10.5 Hz); HRMS, EI for C_8H_{11} ($M - 15^+$) calcd 107.0861, found 107.0867. The IR (neat) had the following bands: 3300 strong (ethynyl hydrogen), 3010 medium (vinyl hydrogen), 2120 weak (triple bond), 1650 weak (double bond), doublet at 1370 and 1390 medium (*gem*-dimethyl), and 705 cm^{-1} strong (cis double bond).

Synthesis of 3,5,5-Trimethyl-2-cyclohexenone Tosylhydrazone. In a 500-mL, round-bottom flask, equipped with a magnetic stirring bar and reflux condenser, was dissolved 27.9 g (0.15 mol) of tosylhydrazine in 200 mL of methanol by stirring the mixture in an oil bath heated to 53 °C. After all the solid had dissolved, 20.7 g (0.15 mol) of 3,5,5-trimethyl-2-cyclohexenone dissolved in 30 mL of methanol was added in one portion. The solution was heated with stirring for 5 h and transferred to an Erlenmeyer flask. Water was added to the warm methanolic solution until it turned cloudy. The flask was scratched with a stirring rod for about 1 min and a solid started to precipitate. The flask was allowed to cool dowm to room temperature and then stored in the freezer overnight. The solid was collected by suction filtration to yield 41.6 g (90%) of a white powdery solid, mp 134–5 °C. The product had the following spectral characteristics: IR (film on NaCl plate) 3220 strong (amine proton), 3025 very weak (vinyl protons), 1650 medium (imine double bond), 1600 medium (double bond), 1370 and 1380 weak (*gem*-dimethyl), 1340 and 1170 strong (sulfonamide), and 820 cm^{-1} (para-substituted benzene); ^1H NMR (20% in $CDCl_3$) singlets at δ 0.85 and 0.95 (6 H, *gem*-dimethyl), two broad peaks with some fine splitting at 1.75 and 1.85 (3 H, methyl on double bond), two broad singlets at 1.90 and 1.95 (2 H, methylene protons on C-4), two sharp singlets at 2.07

Table VII

NaOMe, equiv	A, %	B, %	yield, %
1.2	95.6	4.4	24
1.2	94.0	6.0	17
1.0	96.6	3.4	8
1.0	96.8	3.2	14
1.2	98.2	1.8	11
1.2	97.2	2.8	11

and 2.10 (2 H, methylene protons on C-6), singlet at 2.4 (3 H, methyl on benzene ring), two multiplets at 5.90 and 6.20 (1 H, vinyl proton), two doublets of doublets at 7.3 and 7.9 (5 H, aromatic protons), and a broad peak practically buried underneath the 7.9 doublet (proton on nitrogen, which disappears upon addition of D_2O). The NMR indicates the presence of the two isomers: syn and the anti. Anal. Calcd for $C_{13}H_{22}N_2O_2S$: C, 62.72; H, 7.24. Found: C, 62.57; H, 7.48.

Vacuum Pyrolyses of the Lithium Salt of the 3,5,5-Trimethyl-2-cyclohexenone Tosylhydrazone. Reaction of 1.53 g (5.0 mmol) of tosylhydrazone with 3.7 mL (5.0 mmol) of methyllithium solution afforded the lithium salt which was dried and pyrolyzed at 150 °C in the usual manner. The product was analyzed by GLC on column D at 85 °C and a helium flow rate of 30 mL/min with benzene as an internal standard. The product composition was determined to be 1,5,5-trimethyl-1,3-cyclohexadiene (A) 95.9% and 5,5-dimethyl-1-methylene-2-cyclohexene (B) 4.1%. A second run gave a product composition of 94.5% A and 5.5% B. The yields of products based on tosylhydrazones were 40% for the first and 37% for the second run.

Vacuum Pyrolyses of the Dry Sodium Salt of 3,5,5-Trimethyl-2-cyclohexenone Tosylhydrazone. The dry salt was obtained as previously described employing 1.53 g (5.0 mmol) of tosylhydrazone and pyrolyzed at 150 °C. GLC analyses gave the product compositions shown in Table VII. The salt used in the first two runs was not subjected to the tetrahydrofuran/rotatory evaporator treatment.

Chemical Confirmation of the Structure of the Lithium Salt of 3,5,5-Trimethyl-2-cyclohexenone Tosylhydrazone. A 15.0-mmol sample of the dry lithium salt was prepared in the usual manner. A portion of the dry lithium salt (1.7398 g, 5.57 mmol) was dissolved in 50 mL of water and acidified with several drops of 2 M sulfuric acid (acid to litmus paper). The precipitate was collected by suction filtration to yield 1.5212 g of a white solid. The NMR of the product matched the one of 3,5,5-trimethyl-2-cyclohexenone tosylhydrazone. The amount of product recovered was 89%.

The aqueous phase was extracted with 3 × 10 mL portions of pentane. The combined pentane extracts were dried with magnesium sulfate and concentrated by distillation through a 20-cm Vigreux column. The residue was analyzed by GLC. No peaks corresponding to 1,5,5-trimethyl-1,3-cyclohexadiene or 5,5-dimethyl-1-methylene-2-cyclohexene were detected.

Identification of Products from the Decomposition of the Lithium Salt of 3,5,5-Trimethyl-2-cyclohexenone Tosylhydrazone. The remainder of the above-prepared salt was pyrolyzed and the products collected by preparative GLC. The major compound was identified as 1,5,5-trimethyl-1,3-cyclodexadiene by comparison of its IR and ^1H and ^{13}C NMR with those of an independently synthesized sample. The minor product was identified as 5,5-dimethyl-1-methylene-2-cyclohexene based on its spectral data. The IR (neat) had the following bands: 3075 and 3025 (vinyl hydrogen), 1650 and 1600 medium (conjugated diene), 1360 and 1375 medium (*gem*-dimethyl), 880 strong (gem double bond), and 720 cm^{-1} strong (cis double bond). The ^1H NMR ($CDCl_3$, microcell) had the following peaks: singlet at δ 0.9 (6 H, *gem*-dimethyl), broad singlet at 2.10 (2 H, methylene protons on C-4), broad doublet at 4.8 (2 H, exocyclic vinyl protons), multiplet at 5.7 (1 H, olefinic proton on C-3), and a distorted doublet at 6.1 (1 H, vinyl proton at C-2). The ^{13}C NMR ($CDCl_3$, microcell) had the following peaks: δ 28.35 (*gem*-dimethyl carbons), 29.0 (C-5), 39.81 (C-4), 44.53 (C-6), 111.53 (exocyclic carbon), 139.45 (C-2), and 139.61 (C-3). Carbon 1 was not observed.

Synthesis of 2-Heptanone Tosylhydrazone. In a 250-mL, round-bottom flask equipped with a reflux condenser and a magnetic stirring bar was dissolved 37.2 g (0.20 mol) of tosylhydrazine in 120 mL of methanol by stirring the mixture in an oil bath preheated to 60 °C. To the stirred solution was added 22.8 g (0.20 mol) of 2-heptanone in one portion. The solution was heated at 60 °C for 2.75 h, allowed to cool to room temperature, and treated with water until it turned cloudy. The flask was allowed to stand at room temperature for several hours. The solid was collected by suction filtration to yield 40.4 g of white, lumpy crystals. The mother liquor was stored in the refrigerator overnight to yield a second crop weighing 8.85 g. A total of 49.3 g (87%) of product was obtained, mp 77–8 °C. It showed the following spectral characteristics: IR (solid film) 3200, strong (NH), 1710 weak (C=N), 1330 and 1160 strong (SO_2), and 810 cm^{-1} (para-substituted benzene); ^1H NMR ($CDCl_3$) triplet at δ 0.8 (3 H, terminal methyl), broad multiplet at 1.1 to 1.6 (6 H, internal methylenes), singlet at 1.83 (3 H, methyl next to C=N), triplet at 2.2 (2 H, methylene next to C=N), singlet at 2.5 (3 H, methyl on benzene ring), and a doublet of doublets at 7.30 and 7.90 (5 H, aromatic protons plus the proton on nitrogen buried underneath as evidenced by line sharpening upon addition of D_2O). Anal. Calcd for $C_{14}H_{22}N_2O_2S$: C, 59.55; H, 7.85. Found: C, 59.54; H, 7.74.

Vacuum Pyrolyses of the Dry Lithium Salt of 2-Heptanone Tosylhydrazone. The dry lithium salts were obtained in the usual manner by reaction of 1.42 g (5.0 mmol) of tosylhydrazone with 3.6 mL of 1.4 M (5.0 mmol) methyllithium solution. The salts were pyrolyzed and analyzed by GLC on column B at 55 °C and a 40-mL/min flow rate of helium. Utilizing hexane as an internal standard, the product was determined to consist of 1-heptene (A), *cis*-2-heptene (B), *trans*-2-heptene (C), and 2-heptanone. The alkene distributions are shown below. Besides the alkenes, the product of each run contained 20–30% of 2-heptanone.

T, °C	A, %	B, %	C, %	yield, %
200	3.5	26.6	69.9	3
150	2.9 ± 1.2	34.6 ± 3.2	62.5 ± 2.3	61

Vacuum Pyrolyses of the Dry Sodium Salt of 2-Heptanone Tosylhydrazone. The dry sodium salts were obtained and pyrolyzed at 150 °C in the manner previously described employing 1.42 g (5.0 mmol) of tosylhydrazone. GLC analyses indicated that the product was composed of alkenes A–C; 2-heptanone was not present. The product composition of each run is shown below.

NaOMe, equiv	A, %	B, %	C, %	yield, %
1.0	4.5 ± 2.2	18.9 ± 2.7	76.5 ± 2.6	61
1.6	1.9	14.5	83.6	5
1.6	4.6	16.5	78.9	8

Thermal Decomposition of 2-Heptanone Tosylhydrazone with Sodium Methoxide in Diglyme. The title compound (2.82 g, 10.0 mmol) in dry diglyme was decomposed with 5.10 g (94.3 mmol, 9.4 equiv) of sodium methoxide as previously described. GLC analysis indicated that the alkene distribution was 1.4% A, 15.8% B, and 82.8% C together with a 16% yield of 2-heptanone. The yield of alkenes was 38% based on tosylhydrazone.

Photolysis of the Lithium Salt of 2-Heptanone Tosylhydrazone. The lithium salt of 2-heptanone tosylhydrazone was irradiated in the manner previously described for 2.5 h (50 mL of gas was collected). GLC analysis showed that the alkene composition was 24.2% A, 27.9% B, and 47.9% C in a yield of 6%. The product also contained 2% of heptanone.

Synthesis of 6-Heptyn-2-one Tosylhydrazone. In a 100-mL, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was dissolved 15.1 g (0.081 mol) of tosylhydrazone in 60 mL of methanol by stirring the mixture in an oil bath heated to 51 °C. After all the solid had dissolved, 8.95 g (0.081 mol) of 6-heptyn-2-one[18] was added in one portion. The solution was stirred at 51 °C for 14 h, and then water was added dropwise until the solution turned cloudy. The solution was allowed to cool down to room temperature and then stored in the refrigerator for several hours. The precipitate that had formed was collected by suction filtration to yield 20.30 g (90%) of white crystals, mp 116–117

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°C. The product has the following spectral characteristics: IR (solid film) 3300 (ethynyl hydrogen), 3180 (hydrogen on nitrogen), 1640 (imine double bond), 1600 (aromatic double bond), 1330 and 1160 (sulfonamide), 800 cm^{-1} (para-substituted benzene); ^{1}H NMR (20% in $CDCl_3$) doublet of doublets at δ 7.35 and 7.90 (5 H, aromatic protons on top of NH proton peaks sharpen up after addition of D_2O), singlet at 2.5 (3 H, methyl on benzene ring), triplet at 2.35 (2 H, J = 7 Hz, protons on C-3), multiplet at 2.10 (2 H, protons on C-5), triplet at 1.95 (1 H, J = 2 Hz, ethynyl proton), singlet at 1.80 (3 H, methyl protons of C-1) overlapping with a multiplet at 1.70 (2 H, J = 7 Hz, methylene protons on C-4). Anal. Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52. Found: C, 60.70; H, 6.45.

Vacuum Pyrolyses of the Dry Lithium Salt of 6-Heptyn-2-one Tosylhydrazone. The dry lithium salts were obtained by reaction of 1.39 g of tosylhydrazone with 3.6 mL of a 1.4 M solution of methyllithium as described in the general procedure. The salts were pyrolyzed at 150 °C and analyzed by GLC on column B at 75 °C and a 40-mL/min flow rate of helium employing heptane as the internal standard. The product composition was determined to be 8.1 ± 0.3% of 1-hepten-6-yne (A), 57.3 ± 0.8% of *trans*-5-hepten-1-yne (B), 29.9 ± 2.2% of *cis*-5-hepten-1-yne (C), and 4.8 ± 2.5% of 1-methyl-1,3-cyclohexadiene (D). The yields of products ranged from 13 to 18%.

Vacuum Pyrolyses of the Dry Sodium Salt of 6-Heptyn-2-one Tosylhydrazone. The dry sodium salts were obtained by reaction of 1.39 g (5.0 mmol) of tosylhydrazone with 1.0 equiv of sodium methoxide generated in situ by addition of 0.115 g (5.0 mmol) of sodium to 15 mL of methanol as previously described. The salt was pyrolyzed at 150 °C and analyzed by GLC. The product composition was determined to be 5.9 ± 0.7% A, 35.1 ± 1.7% B, 11.4 ± 1.6% C, and 47.8 ± 2.2% D. The yields of products were 3 to 4%. To test the stability of the products to the reaction conditions, a product fraction (46.9% **11b**, 5.3% **21**, 37.0% **23**, and 10.8% **22**) was added to the pot residue from the above reaction and the mixture heated at 150 °C for 2 min; the volatile fraction was then allowed to distill into a trap at 4 mm pressure and GLC analysis of this fraction revealed a composition of 44.1% **11b**, 5.8% **21**, 38.4% **23**, and 11.7% **22**. The observed reaction time in the original pyrolysis was less than 30 s.

Photolysis of the Lithium Salt of 6-Heptyn-2-one Tosylhydrazone. The lithium salt was generated employing the experimental procedure cited earlier by reacting 0.70 g (2.50 mmol) of tosylhydrazone with 1.5 mL of a 1.67 M solution of methyllithium (2.5 mmol). The solution was irradiated for 4.0 h and 36 mL of nitrogen was collected (66% of the theoretical amount). The residue was analyzed by GLC. The product composition was determined to be 15.4% A, 27.1% B, 18.0% C, and 39.5% D. The yield of product was 2%.

Identification of Products from the Reactions of 6-Heptyn-2-one Tosylhydrazone. The products of the vacuum pyrolysis of the lithium salt of 6-heptyn-2-one tosylhydrazone were isolated by preparative GLC and identified by their spectral properties. The first peak was identified as 1-hepten-6-yne. The IR (neat) had the following bands: 3300 strong (ethynyl hydrogen), 3060 weak (vinyl hydrogen), 2125 weak (triple bond), 1650 medium (double bond), 995 medium, and 910 cm^{-1} strong (characteristic bands for a terminal olefin). The ^{1}H NMR ($CDCl_3$) exhibited the following peaks: ^{1}H NMR ($CDCl_3$) δ 1.63 (P, 2 H, J = 7 Hz, C-4), 1.95 (t, 1 H, J = 2 Hz, C-7), 2.09–2.20 (m, 4 H, C-3, C-5), 4.97–5.08 (3 bs, 2 H, C-1), 5.72–5.82 (m, 1 H, C-2); HRMS, EI for C_7H_9 (M – 1$^+$) calcd 93.0704, found 93.0714. The third peak was identified as *cis*-5-hepten-1-yne based on the following spectral characteristics: IR (neat) 3300 strong (ethynyl hydrogen), 3020 medium (vinyl hydrogen), 2125 (triple bond), 1650 weak (double bond), and 730 cm^{-1} strong (characteristic of cis olefin); ^{1}H NMR ($CDCl_3$) δ 1.63 (d, 3 H, J = 6.5 Hz, C-7), 1.95 (t, 1 H, J = 2 Hz, C-1), 2.19–2.31 (m, 4 H, C-3, C-4), 5.41–5.61 (m, 2 H, C-5, C-6). Decoupling δ 1.63 yielded δ 5.55 (d, 1 H, J = 10.5 Hz, C-6); HRMS, EI for C_7H_9 (M – 1$^+$) calcd 93.0704, found 93.0684. The second peak was identified as *trans*-5-hepten-1-yne based on the following spectral characteristics: IR (neat) 3300 strong (ethynyl hydrogen), 3040 medium (vinyl hydrogen), 2130 weak (triple bond), 1650 weak (double bond), and 965 cm^{-1} strong (characteristic of a trans olefin); ^{1}H NMR ($CDCl_3$) δ 1.66 (d, 3 H J = 6.5 Hz, C-7), 1.96 (t, 1 H, J = 2 Hz, C-1), 2.16–2.26 (m, 4 H, C-3, C-4), 5.43–5.58 (m, 2 H, C-5, C-6). Decoupling δ 1.66 yielded δ 5.52 (d, 1 H, J = 15.5 Hz, C-6); HRMS, EI for C_7H_9 (M – 1$^+$) calcd 93.0704, found 93.0714.

The fourth product, 1-methyl-1,3-cyclohexadiene, was identified by comparison of its retention time and spectra with those of an independently synthesized sample.

Synthesis of 3-Methyl-2-cyclohexenone Tosylhydrazone. In a 100-mL, round-bottom flask equipped with a magnetic stirring bar and a reflux condenser was dissolved 9.31 g (0.050 mol) of tosylhydrazine in 30 mL of methanol by heating to 44 °C (oil bath) for about 10 min. After all the solid had dissolved, 5.51 g (0.050 mol) of 3-methyl-2-cyclohexenone was added in one portion. The solution was heated at 44 °C for 50 min (it turned dark yellow), allowed to cool down to room temperature, and stored in the refrigerator overnight. The precipitate that formed was collected by suction filtration to yield 9.50 g (68%) of a white powder with a slight brownish tinge, mp 144–6 °C. The product exhibited the following spectral characteristics: IR (solid film) 3200 strong (amine hydrogen), 3030 weak (vinyl hydrogen), 1650 medium (conjugated carbon–nitrogen double bond), 1600 medium (conjugated carbon–carbon double bond), 1590 shoulder and 1490 weak (aromatic double bonds), 1330 strong and 1170 strong (sulfonamide), 820 cm^{-1} strong (para-substituted benzene); ^{1}H NMR (20% in $CDCl_3$) distorted triplet at δ 1.8 (3 H, methyl protons of the carbon attached to C-3 of the cyclohexene ring), multiplet from 1.95 to 2.4 (6 H, methylene protons of C-4, -5, and -6 of the cyclohexene ring), singlet at 2.45 (3 H, methyl protons of the benzylic carbon), broad singlets with fine splitting at 5.95 and 6.20 (1 H, vinyl proton, syn and anti isomers), doublet of doublets at 7.25 and 7.8 (5 H, aromatic protons with the amine proton buried underneath the doublet at δ 7.8 as evidenced by line sharpening upon exchange with D_2O). Anal. Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52. Found: C, 60.00; H, 6.28.

Synthesis of 1-Methyl-1,3-cyclohexadiene. The method used for the synthesis of 1,5,5-trimethyl-1,3-cyclohexadiene was employed. A solution of 2.79 g (10.0 mmol) of 3-methyl-2-cyclohexenone tosylhydrazone in 50 mL of dry ether under nitrogen was allowed to react with 13.7 mL of a 1.75 M solution of methyllithium (24.0 mmol), 2.40 equiv). The residue obtained after workup and removal of solvent through a 20-cm Vigreux column was analyzed by GLC on column C at 80 °C and a helium flow rate of 50 mL/min. The GLC trace indicated the presence of a major product plus a small amount of an impurity. The major product was obtained by preparative GLC. It had the following spectral properties: IR (neat) 3030 strong (vinyl hydrogen), 1650 weak and 1600 (double bond, characteristic of conjugated diene), 840 (trisubstituted olefin), 690 cm^{-1} (cis olefin); ^{1}H NMR (20% in $CDCl_3$) broad singlet at δ 1.8 (3 H, methyl protons), broad singlet with some fine splitting at 2.2 (4 H, methylene protons of carbons 5 and 6), broad multiplets at 5.7 (2 H, vinyl protons), and a broad multiplet at 5.9 (1 H, vinyl proton); ^{13}C NMR (20% in $CDCl_3$) δ 22.80 (methyl carbon attached to double bond), 23.39 (C-5), 27.98 (C-6), 119.06 (C-4), 122.98 (C-2 or -3), 124.69 (C-3 or -2), and 135.87 (C-1).